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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : G01N 21/55 — A1

(11) International Publication Number: WO 93/14393

(43) International Publication Date: 22 July 1993 (22.07.93)

(21) International Application Number: PCT/GB93/00027

(22) International Filing Date: 8 January 1993 (08.01.93)

(30) Priority data:
9200563.6 11 January 1992 (11.01.92) GB

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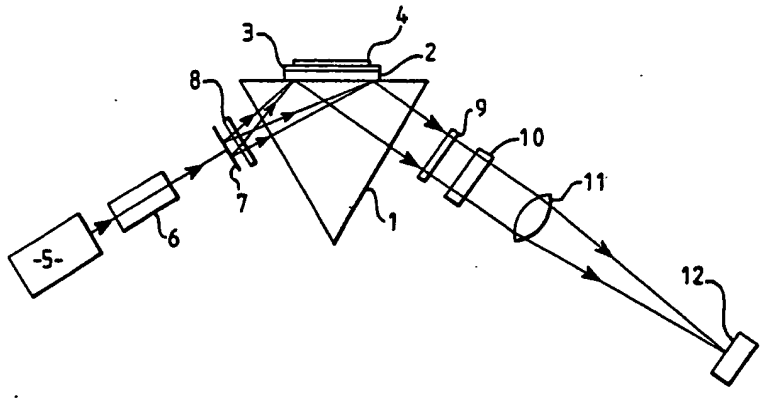
(81) Designated States: JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: ANALYTICAL DEVICE WITH LIGHT SCATTERING



(57) Abstract

Apparatus for the determination of a chemical or biochemical species comprises a resonant optical sensor (1-4) disposed in a light path between a source (5) of monochromatic light and a detector (12) adapted to monitor some characteristic of the light. A light-scattering element (7) is disposed in the light path between the source (5) and the sensor (1-4). The light-scattering element may be a speckle plate or a diffusion screen, and is preferably formed on the input side of the sensor, which may be a disposable unit.

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Title : Analytical Device with Light Scattering

This invention relates to sensors, especially those termed biosensors, ie devices for the analysis of biologically active species such as antigens and antibodies in samples of biological origin. In particular, the invention relates to biosensors based on resonant optical phenomena, eg surface plasmon resonance or resonant attenuated or frustrated total internal reflection.

Many devices for the automatic determination of biochemical analytes in solution have been proposed in recent years. Typically, such devices (biosensors) include a sensitised coating layer which is located in the evanescent region of a resonant field. Detection of the analyte typically utilizes optical techniques such as, for example, surface plasmon resonance (SPR), and is based on changes in the thickness and/or refractive index of the coating layer resulting from interaction of that layer with the analyte. This causes a change, eg in the angular position of the resonance.

Other optical biosensors include a waveguide in which a beam of light is propagated. The optical characteristics of the device are influenced by changes occurring at the surface of the waveguide. One form of optical biosensor is based on frustrated total reflection. The principles of frustrated total reflection (FTR) are well-known; the technique is described, for example, by Bosacchi and Oehrle [Applied Optics (1982), 21, 2167-2173]. An FTR device for use in immunoassay is disclosed in European Patent Application No 2205236A and comprises a cavity layer bounded on one side by the sample under investigation and on the other side by a spacer layer which in turn is mounted on a substrate. The substrate-spacer layer interface is irradiated with monochromatic radiation such that total reflection occurs, the associated evanescent field penetrating through the spacer layer. If the thickness of the spacer layer is correct and the incident parallel wave

vector matches one of the resonant mode propagation constants, the total reflection is frustrated and radiation is coupled into the cavity layer. The cavity layer must be composed of material which has a higher refractive index than the spacer layer and which is transparent at the wavelength of the incident radiation.

In devices of this kind, the position of resonance may be monitored by scanning the angle at which monochromatic light is incident on the sensor. The scanning of angle may be performed either sequentially or simultaneously ie by varying the angle of incidence of a parallel beam of light or by simultaneously irradiating over a range of angles using a fan-shaped beam of light as described (in connection with SPR) in European Patent Application No 0305109A. In the first configuration, prior proposals have involved a single-channel detector which is mechanically scanned over a range of angles; this necessitates synchronisation of the movement of the light source and the detector. The second configuration, in which a range of angles is irradiated simultaneously, requires relatively complex optics, which leads to relatively high manufacturing costs.

There has now been devised an apparatus involving the use of a resonant optical sensor for the determination of a chemical or biochemical species, which overcomes or substantially mitigates some or all of the disadvantages of the prior art arrangements described above.

According to the invention, there is provided apparatus for the determination of a chemical or biochemical species, comprising a resonant optical sensor disposed in a light path between a source of monochromatic light and a detector adapted to monitor some characteristic of the light, a light-scattering element being disposed in the light path between the source and the sensor.

The apparatus according to the invention is advantageous primarily in that it enables simultaneous irradiation at a range of angles, yet is of relatively simple and inexpensive construction, eg due to the absence of complex optics.

Any convenient source of monochromatic light may be used but it is preferable to use a laser. The choice of laser will depend inter alia on the particular form of sensor used. In this context, 'light' may include not only visible light but also wavelengths above and below this range, eg in the ultra-violet and infra-red.

The light-scattering element is preferably a speckle plate or diffusion screen. To overcome the problem of speckle being transferred to the output, it may be necessary to translate or rotate the speckle plate rapidly, ie quicker than the integration time of the detector.

The speckle plate may be a separate component or it may be formed integrally with another component, eg as the output side of a half-wavelength plate comprising a mica sheet sandwiched between two glass sheets.

In a particularly preferred embodiment, the light-scattering element is formed on the input side of the sensor, eg where the sensor is formed as a disposable unit. In this case, the light source can be located very close to the sensor, enabling the use of a compact and inexpensive light source such as a laser diode.

The characteristic of the light which is monitored may be any characteristic which changes at resonance, eg the phase of reflected radiation or, in some cases, the intensity.

The sensor is preferably an FTR sensor. Such a sensor will generally include an optical structure comprising

a) a cavity layer of transparent dielectric material of

refractive index n_3,

b) a dielectric substrate of refractive index n_1, and

c) interposed between the cavity layer and the substrate, a dielectric spacer layer of refractive index n_2.

In use, the interface between the substrate and the spacer layer is irradiated with light such that internal reflection occurs. Resonant propagation of a guided mode in the cavity layer will occur, for a given wavelength, at a particular angle of incidence.

The wavelength at which the resonant effect occurs depends on various parameters of the sensor device, such as the refractive indices and thicknesses of the various layers. In general, it is a pre-requisite that the refractive index n_3 of the cavity layer and the refractive index n_1 of the substrate should both exceed the refractive index n_2 of the spacer layer. Also, since at least one mode must exist in the cavity to achieve resonance, the cavity layer must exceed a certain minimum thickness.

The cavity layer is preferably a thin-film of dielectric material. Suitable materials for the cavity layer include zirconium dioxide, titanium dioxide, aluminium oxide and tantalum oxide.

The cavity layer may be prepared by known techniques, eg vacuum evaporation, sputtering, chemical vapour deposition or in-diffusion.

The dielectric spacer layer must have a lower refractive index than both the cavity layer and the substrate. The layer may, for example, comprise an evaporated or sputtered layer of magnesium fluoride. Other suitable materials include lithium fluoride and silicon dioxide. Apart from the evaporation and sputtering techniques mentioned above, the spacer layer may be deposited on the substrate by a sol-gel process, or be formed

by chemical reaction with the substrate.

The sol-gel process is particularly preferred where the spacer layer is of silicon dioxide.

The refractive index of the substrate (n_1) must be greater than that (n_2) of the spacer layer but the thickness of the substrate is generally not critical.

By contrast, the thickness of the cavity layer must be so chosen that resonance occurs within an appropriate range of coupling angles. The spacer layer will typically have a thickness of the order of several hundred nanometres, say from about 200nm to 2000nm, more preferably 500 to 1500nm, eg 1000nm. The cavity layer typically has a thickness of a few tens of nanometres, say 10 to 200nm, more preferably 30 to 150nm, eg 100nm.

It is particularly preferred that the cavity layer has a thickness of 30 to 150nm and comprises a material selected from zirconium dioxide, titanium dioxide, tantalum oxide and aluminium oxide, and the spacer layer has a thickness of 500 to 1500nm and comprises a material selected from magnesium fluoride, lithium fluoride and silicon dioxide, the choice of materials being such that the refractive index of the spacer layer is less than that of the cavity layer.

Preferred materials for the cavity layer and the spacer layer are tantalum oxide and silicon dioxide respectively.

At resonance, the incident light is coupled into the cavity layer by FTR, propagates a certain distance along the cavity layer, and couples back out (also by FTR). The propagation distance depends on the various device parameters but is typically of the order of 1 or 2mm.

At resonance the reflected light will undergo a phase change,

and it is this which may be detected.

In general, it is necessary for suitable optical components to be used to prevent non-resonant reflected light reaching the detector. This prevents the technique being used with conventional SPR, or with FTR as described in our co-pending International Patent Application No PCT/GB91/01161 in which the cavity layer and/or spacer layer absorbs at resonance, unless augmented with suitable optics as described in our co-pending International Patent Application No PCT/GB91/01466.

For use in the determination of biochemical species, the surface of the sensor, ie the surface of the cavity layer in the case of an FTR sensor, will generally be sensitised by having biomolecules, eg specific binding partners for the analyte(s) under test, immobilised upon it. The immobilised biochemicals may be covalently bound to the sensor surface by methods which are well known to those skilled in the art.

The invention will now be described in more detail, by way of illustration only, with reference to the accompanying drawings in which

Figure 1 is a schematic view (not to scale) of an apparatus according to the invention,

Figure 2 depicts the dependence of the intensity of the detected light on the angle of incidence, and

Figure 3 is a schematic view of part of a second embodiment of an apparatus according to the invention.

Referring first to Figure 1, a biosensor comprises a glass prism 1 coated over an area of its base with a first coating 2 of magnesium fluoride and a second coating 3 of titanium dioxide. The prism 1 and first and second coatings 2,3 together constitute a resonant optical structure, the first

coating 2 acting as a spacer layer and the second coating 3 as a cavity layer. The first coating 2 has a thickness of approximately 1000nm and the second coating 3 a thickness of approximately 100nm.

Immobilised on the surface of the second coating 3 is a layer 4 of immobilised biochemicals, which act as specific binding partner for the analyte under test.

The interface between the base of the prism 1 and the first coating 2 is irradiated by a beam of monochromatic light from a laser 5. Light from the laser 5 is collimated by optics 6 and passes through a speckle plate 7 and a polariser 8.

The polariser 8 is arranged to produce linearly polarised light with two components : transverse electric (TE) and transverse magnetic (TM). The polariser is set at 45° to the TE and TM transmission axes and thus provides equal components of TE and TM light.

The laser 5 is arranged to maximise the intensity of the light transmitted through the polariser 8 ie with the polarisation axis aligned with that of the polariser 8.

The effect of the speckle plate 7 is to present light at a range of angles (including the angle at which resonance occurs) across the whole length of the interface between the base of the prism 1 and the first coating 2. This is a major advantage of this technique, avoiding errors due to imperfections such as dust or scratches on the surface as may occur when a narrow beam of light is used.

All the light incident on the interface between the base of the prism 1 and the first coating 2 is reflected, resonance being detected as a change of phase of the reflected light.

The reflected light is passed through a compensator 9 to a

polarisation analyser 10. The compensator 9, which may be of any conventional form, is manually adjusted to remove any phase difference which is introduced into the TE and TM components on reflection and by birefringence in the optical path.

Away from the resonant angle, the compensator 9 is adjusted to allow for the difference in phase change occurring on reflection of the TE and TM components. An approximately plane-polarised beam of light is therefore incident on the analyser 10 and this is adjusted to give zero transmission to a detector 12. This will apply for all angles except near resonance. Near resonance of either component, the phase shift produced by reflection will vary rapidly with angle, resulting in maximum throughput of light through the analyser 10 at resonance.

Light passing through the analyser 10 is focussed by a cylindrical lens 11 onto a detector 12. The lens 11 is telecentric, ie located at one focal length from the prism 1 and one focal length from the detector 12. This minimises the effects of positioning errors.

In use, light is incident on the interface between the base of the prism 1 and the first coating layer 2 simultaneously at a range of angles, including the resonant angle. Off-resonance no light intensity is detected at the detector 12; as resonance is approached, the detected light intensity increases and then falls.

When the layer of immobilised biochemicals 4 is contacted with a sample containing the analyte under test, specific binding occurs between the biochemicals and the analyte molecules, resulting in a change in the refractive index in the vicinity of the surface of the device. This in turn results in a shift in the position of the resonance. Figure 2 shows a plot of the measured signal intensity against angle before and (dotted

line) after complexation of the immobilised biochemicals with the analyte.

In the embodiment shown in Figure 3, the resonant optical sensor (comprising the layers 2,3,4) is formed on a disposable glass block 31, the input window 32 of which is formed as a diffusion screen. The light source is a laser diode 33 located, in use, very close to the screen 32 and aligned so as to give the major plane of polarisation at 45° to the TE and TM transmission axes.

Claims

1. Apparatus for the determination of a chemical or biochemical species, comprising a resonant optical sensor (1-4) disposed in a light path between a source (5) of monochromatic light and a detector (12) adapted to monitor some characteristic of the light, a light-scattering element (7) being disposed in the light path between the source (5) and the sensor (1-4).

2. Apparatus as claimed in Claim 1, wherein the source (5) of monochromatic light is a laser.

3. Apparatus as claimed in Claim 1 or Claim 2, wherein the light-scattering element is a speckle plate (7).

4. Apparatus as claimed in Claim 1 or Claim 2, wherein the light-scattering element is a diffusion screen.

5. Apparatus as claimed in Claim 3, wherein the speckle plate can be translated or rotated more quickly than the integration time of the detector.

6. Apparatus as claimed in any preceding claim, wherein the speckle plate is formed integrally with another component, eg as the output side of a half-wavelength plate comprising a mica sheet sandwiched between two glass sheets.

7. Apparatus as claimed in any one of Claims 1 to 5, wherein the light-scattering element (32) is formed on the input side of the sensor (31).

8. Apparatus as claimed in Claim 7, wherein the sensor (31) is a disposable unit.

9. Apparatus as claimed in Claim 8, wherein the source of monochromatic light is a laser diode (33).

10. Apparatus as claimed in any preceding claim, wherein the sensor (1-4) is an FTR sensor comprising

a) a cavity layer (3) of transparent dielectric material of refractive index n_3,

b) a dielectric substrate (1) of refractive index n_1, and

c) interposed between the cavity layer (3) and the substrate (1), a dielectric spacer layer (2) of refractive index n_2.

United States Patent Application

Title Process for Recovery of Hydrocarbon Oils from Oil Shale and Other Carbonaceous Solids

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ABSTRACT

An innovative, continuous, surface process and equipment for thermal recovery of hydrocarbon oils from oil shale and/or other carbonaceous solids is disclosed herein. The premises for this patent include (1) a simple process with mild operating conditions and with as many components as possible being standard, available equipment, (2) use of coal or other low cost solid hydrocarbon fuel including spent shale and shale fines to provide for process energy requirements. (3) A self-contained process that produces hydrogen for on-site shale oil upgrading to transportation fuel. (4) An energy-efficient process to maximize the production of shale oil per ton of coal or other feedstock energy source while minimizing other products such as electrical energy. It is intended that this process be energy-efficient, low cost and with reduced time to construct and demonstrate for commercial operation. In this process, one alternative is the use of conventional gasification of coal, which provides (1) hydrogen for product oil upgrading, (2) allowance for removal and use or disposal of CO_2 and (3) a remaining synthetic gas (e.g., CO, hydrocarbons) for rotary kiln thermal requirements to liberate the shale oil. Direct combustion of this synthetic gas maximizes the shale oil production and simplifies the process by eliminating components for processing the syngas. Combustible kiln off-gas after shale oil condensation, carbon-containing spent shale, shale fines, and hot kiln combustion off-gases can readily meet additional thermal requirements, such as kiln steam production and coal, oxygen and shale preheating requirements. The process is environmentally compliable and produces transportation-quality liquids on-site, by hydrotreating of the oil shale.

INTRODUCTION

In this process, as applied to oil shale, the rock is mined, delivered to the plant and stockpiled, crushed to designed size and fed to a rotary kiln or other surface reactor. Coal or other solid carbonaceous energy source is mined, delivered to the plant, stockpiled, crushed to designated size and typically gasified in a steam and oxygen in a standard, coal gasifier. Crushed shale fines, too small for kiln use, can be combined with the coal and gasified. The gasification products are cooled, the particulate matter (coal ash), the contaminant gases (e.g., S) are removed, and the hydrogen removed for subsequent shale oil upgrading. If required, the CO_2 can also be removed. The remaining syngas (i.e., CO, some hydrocarbons) is combusted with air for use in the indirectly fired kiln to recover the oil from the shale. The syngas combustion products are cleaned to meet environmental requirements. The spent shale from the kiln is separated from the

gas/vapor stream which is then cooled to condense the shale oil product. The carbon in the spent shale and the combustible hydrocarbons in the kiln gas are available for preheating the shale feedstock to the kiln and for producing steam for the gasifier and for the kiln carrier gas. The shale oil is hydrotreated and hydrocracked on-site with the product hydrogen from the gasifier to produce a transportation-ready fuel.

Claim 1

A continuous surface process for thermally removing condensable liquid hydrocarbons from solid feedstocks such as oil shale or tar sands in a thermally efficient, self-contained, environmentally sound and simple process comprising the steps of:

a. Preparing the mined shale or other feedstock to specified size and moisture level.
b. Preparing and gasifying a hydrocarbonaceous solid feedstock such as coal to provide thermal requirements for the shale oil recovery and hydrogen requirements for product oil (such as shale oil) on-site upgrading.
c. Processing the gasifier syngas for particulate and contaminant removal, and hydrogen removal.
d. Combusting the remaining syngas with air for thermal use in an indirectly-heated rotary kiln, or other reactor at atmosphere or near-atmosphere pressure.
e. Preheating water or other kiln sweep gas and preheating shale feedstock for entry into the kiln using available thermal sources such as spent shale, kiln off-gas or kiln combustion effluent gas.
f. Feeding the crushed oil shale into the kiln or other reactor to thermally liberate the shale oil which is removed from the kiln by the flowing sweep gas.
g. Condensing the shale oil product with coolant such as cool water from the kiln sweep gas and collecting remaining off-gas for process thermal uses.
h. Hydrotreating and hydrocracking the shale oil product with the on-site produced hydrogen to produce a ready transporation liquid tailored to specification.

Claim 2

The process of claim 1 where spent shale is circulated to the gasifier and combined to the coal or other solid feedstock for gasification.

Claim 3

The process of claim 1 where the unused shale fines left from grinding and screening are circulated to the gasifier and combined with the other feedstocks (e.g., coal).

Claim 4

The process of claim 1 where the gasifier is a commercially available unit of proper capacity, of the entrained, fixed or fluidized bed type.

Claim 5

The process of claim 1 where CO_2 is removed from the gasifier syngas to reduce atmosphere CO_2 emissions.

Claim 6

The process of claim 1 where the hydrogen for hydrotreating the shale oil is delivered to the site.

Claim 7

The process of claim 1 where no gasifier is used and where combustible fuel such as coal, natural gas, gilsonite, spent shale or shale fines is burned directly and required hydrogen is delivered to the site.

Claim 8

The process of claim 1 where the reactor for thermally removing the oil from shale is stationary (non-rotating) with a solid screw feed system and transport system.

Claim 9

The process of claim 1 where the reactor or kiln is operated at elevated pressure to increase capacity.

Claim 10

The process of claim 1 where CO_2 gas is captured from the gasifier syngas prior to it's being burned to provide thermal energy for kiln operation.

Claim 11

The process of claim 1 where the available excess by products containing thermal energy (e.g) (spent shale carbon, shale fines, kiln off-gas) are burned to generate electrical energy for on-site use or to deliver the electrical energy for off-site use.

Claim 12

A method for thermally removing condensable hydrocarbons from solid feedstock such as oil shale or tar sands comprising the steps of:

(dependent claims to follow like the list for Claim 1)

Claim 13

A continuous surface process for thermally removing condensable liquid hydrocarbons from solid feedstocks such as oil shale or tar sands in a thermally efficient environmentally sound and sample process comprising the steps of:

a. Preparing the mined shale or other feedstock to specified size and moisture level.
b. Combusting the spent shale, kiln off gas or shale fines to providing thermal energy requirements for operating the indirectly-heated rotary kiln or other heater at atmospheric or near atmospheric pressure.
c. Feeding the crushed oil shale into the kiln or other reactor to thermally lliberate the shale oil which is removed from the kiln by the following sweep gas.
d. Preheating water or other kiln sweep gas and preheating shale feedstock for entry into the kiln using available thermal sources such as spent shale, kiln off-gas or kiln combustion effluent gas.
e. Condensing the shale oil product with coolant such as cool water from the kiln sweep gas and collecting remaining off-gas for process thermal uses.
f. Steam reforming a solid, liquid or gaseous feedstock such as gilsonite, petroleum, natural gas to provide on-site hydrogen for upgrading shale oil quality.
g. Hydrotreating and hydrocracking the shale oil product with the on-site produced hydrogen to produce a ready transporation liquid tailored to specification.

(include dependent claims)

Claim 14

a. Preparing the mined shale or other feedstock to specified size and moisture level.
b. Combusting the spent shale, kiln off gas or shale fines to providing thermal energy requirements for operating the indirectly-heated rotary kiln or other heater at atmospheric or near atmospheric pressure.
c. Feeding the crushed oil shale into the kiln or other reactor to thermally lliberate the shale oil which is removed from the kiln by the following sweep gas.
d. Preheating water or other kiln sweep gas and preheating shale feedstock for entry into the kiln using available thermal sources such as spent shale, kiln off-gas or kiln combustion effluent gas.
e. Condensing the shale oil product with coolant such as cool water from the kiln sweep gas and collecting remaining off-gas for process thermal uses.

f. Steam reforming a solid, liquid or gaseous feedstock such as gilsonite, petroleum, natural gas to provide on-site hydrogen for upgrading shale oil quality.
g. Hydrotreating and hydrocracking the shale oil product with the on-site produced hydrogen to produce a ready transporation liquid tailored to specification.

Then:

h. Process the near-carbon free spent shale fines, which contain high carbonate percentages to produce marketable cement.